Renewable and Sustainable Energy Reviews 39 (2014) 24–34

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A review on potential enzymatic reaction for biofuel production from algae

M.Y. Noraini [a], Hwai Chyuan Ong [a,b,*], Mohamed Jan Badrul [b,c], W.T. Chong [a,b]

[a] Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[b] Centre for Energy Sciences, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
[c] Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

ARTICLE INFO

Article history:
Received 13 February 2014
Received in revised form
10 May 2014
Accepted 7 July 2014

Keywords:
Algae
Biofuel
Enzymatic reaction
Alternative energy
Biodiesel
Bioethanol

ABSTRACT

Increasing number of population, advanced technology and economics growth somehow has caused energy depletion. The development of biofuel such as biodiesel, bioethanol and biogas is extremely needed to overcome these crises. Biofuel is derived from biological sources or biomass which are more environmental friendly, less toxic, reduce greenhouse gas emission and less cost. Algae comes from the third generation product of both biodiesel and bioethanol. Algae based biofuel has various advantages such as non-toxic, does not require fresh water to grow, higher growth rate, biodegradable and not used arable land. Thus, this review summarizes enzymatic reaction for production of all biofuels; biodiesel and bioethanol. The enzymatic reaction is safe, less contaminating and seems to produce higher yield of biofuel compared to chemical reaction. Overall finding of this study suggests that immobilization method and efficiency of the enzyme is the main factor in biofuel production. Finally, further studies are recommended to overcome the major constraint of high enzyme cost by improving the immobilization technique and processes.

Contents

1. Introduction

It is not a secret that fossil fuels are the main source of energy for the world and attract millions of users in many applications and sectors such as business, transportation, research, and industries. There are three major forms of fossil fuels: coal, oil and natural gas which were formed hundred millions years ago. However, fossil fuel is not infinite and there are many challenges faced by societies such as energy security, increase of oil price, resource depletion, and climate change that lead researchers to search for new and attractive sources to replace the fossil fuels [1]. Biofuel is one of the alternatives derived from various renewable biological sources such as algae, soybean, jatropha, corn, palm, coconut, rice bran, linseed, jojoba, castor and waste [2]. Production and usage of biofuel are not new. Vegetable oil has been used in an engine during 1930s in emergency cases [3]. Currently, three types of biofuels have been discussed extensively by other researchers; which are biodiesel, bioethanol and biohydrogen. There are many improvements and research focused to enhance the quality of a biofuel that is feasible and safe for consumers. According to the

* Corresponding author. Tel.: +60 16 5903110; fax: +60 3 7967 5317.
E-mail addresses: onghc@um.edu.my, ong1983@yahoo.com (H.C. Ong).

http://dx.doi.org/10.1016/j.rser.2014.07.089
1364-0321/

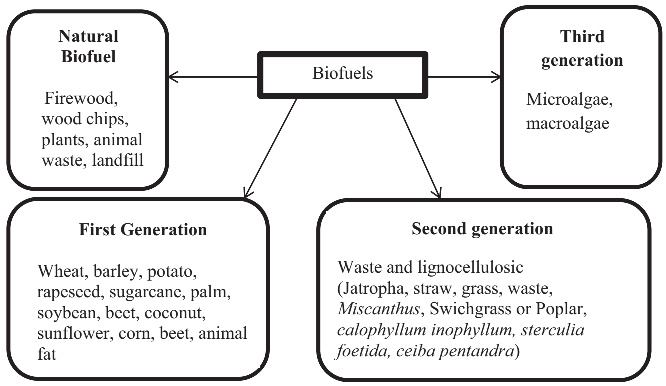

Fig. 1. Generation of biofuels.

reports of international agencies roughly 53% increase in the demand of energy is expected by the year 2030 [4]. According to this statistic, world consumption of petroleum is 89.41 million barrels per day in 2012 [5] and will increase to 136.80 million barrels per day by 2030. Malaysia is the second largest oil and natural gas producer in Southeast Asia, also the second largest exporter of liquefied natural gas globally. Malaysia's production of petroleum is expected to reach 700 thousand barrels per day and consumption of petroleum, 598 thousand barrels per day in 2014 [5].

Biofuels has several classifications, namely natural biofuel, first generation, second generation and third generation as shown in Fig. 1. Natural biofuels are generally derived from organic sources such as vegetables, animal waste and landfill gas [6]. The natural biofuels is commonly used for cooking, heating, brick kiln or electricity production. On the other hand, first generations of biofuel are derived from edible feedstock like wheat, palm, corn, soybean, sugarcane, rapeseed, oil crops, sugar beet and maize [7]. It is expected that the growth in production and consumption of biofuels are increasing, but their impacts towards meeting the overall energy demands in the transport sector will remain limited. This is mainly because of the competition with food and fiber production for the use of arable land, regionally constrained market structures, lack of well managed agricultural practices in emerging economies, high water and fertiliser requirements, and a need for conservation of bio-diversity [8]. Thus, the first generation is claimed to be not very successful since it affects food security and global food markets.

Furthermore, waste and dedicated lignocellulosic feedstocks such as *Miscanthus*, jatropha, *Sterculia foetida*, *Ceiba pentandra*, Swichgrass or Poplar are known as second generation of biofuels [7,9]. This generation of biofuels brings many more advantages compared to the first generation due to higher yield and lower land requirement. The major drawback is the lack of efficient technologies for commercial applications [7]. Third generation of biofuels uses macro- and micro-algae as feedstock and it is seen as a technically viable alternative energy approach that may overcome the major drawbacks associated with the first and second generation biofuels [8]. Numerous advantages have been highlighted for the fuel production from algae such as high growth rate, high efficiency CO_2 mitigation, less water demand than land crops and more cost effective farming [10].

To date, most reviews emphasized on the production of biofuel, technologies [8], processes [11] and potential of variable feedstocks such as algae for biofuel production [12]. These reports focus merely on the advantages of the feedstocks, techniques, processes for biodiesel and bioethanol. As yet, no review has been written about enzyme-catalyzed reaction for biodiesel production from microalgae. Therefore, this review is aimed to fill this gap and summarize about the extraction of biofuels such as biodiesel and bioethanol from algae by enzyme-catalyzed reaction.

Table 1
Comparison of elemental and chemical content of biodiesel and diesel [19].

Components	Biodiesel content (%)	Diesel content (%)
Carbon	79.6	86.4
Hydrogen	10.5	13.6
Oxygen	8.6	–
Nitrogen	1.3	–
C/H	7.6	6.5
n-aliphatics	15.2	67.4
Olephenics	84.7	3.4
Aromatics	–	20.1
Naphtens	–	9.1

2. Biodiesel

Biodiesel is usually defined as methyl (or ethyl) esters of fatty acids obtained by transesterification (alcoholysis) of triglycerides. Typically, biodiesel encompasses alkyl fatty acid (chain length C_{14}–C_{22}) esters of short-chain alcohols, primarily, methanol or ethanol. Biodiesel has the most compatible characteristics with the fossil fuel due to its higher heating value, flash point, cetane number and kinematic viscosity [13]. Biodiesel is one of the most demanding fuels to support limited supply of fossil fuels in future. In addition, the utmost characteristics of biodiesel is abundance; it is environmental friendly, its reduces net carbon-dioxide emissions by 78% [14–16], it is renewable, non-toxic, non-flammable, and biodegradable [4,17,18]. Moreover, higher flash point of vegetable oils, makes their storage, transportation and handling easier. Biodiesel is also 66% better than petrodiesel when used as lubricant [13].

Biodiesel has more polar structure based on the oxygen level compared to diesel as shown in Table 1. Therefore biodiesel has higher viscosity for lower heating value compared to diesel fuel [19]. Biodiesel can be used in its pure form or mixed with certain proportions of diesel such as B20 which contains 20% biodiesel and 80% diesel.

There are several methods to extract and esterifies vegetable oil or animal fats into biodiesel. It could be extracted chemically using solvent such as hexane or benzene [14,20]. It can also be extracted physically either by using oil press, osmotic shock or ultrasound [21]. In order to esterify the oil into fatty acid methyl ester (FAME), few methods have been applied and studied to enhance the efficiency of biodiesel. Among the popular method are acid-catalyzed transesterification, alkali-catalyzed transesterification, enzymatic transesterification followed by supercritical ethanol [22], supercritical carbon dioxide, microwave, and ultrasound transesterification [23]. The latest technology in biodiesel production including wet lipid extraction [24], continuous heterogeneous catalyzed process or McGyan® process [20,25] and enzymatic conversion in ionic liquid [26]. In McGyan® process reported by Krohn et al. a biomass of wild culture, Kelp, *Dunaliella tertiolecta* and *Nannochloropsis oculata* was converted to biodiesel at 85% efficiency [20].

The conventional process for biodiesel production is transesterification of oil and alcohol using catalysts or supercritical conditions with or without presence of catalyst. Yet, the usage of homogeneous catalyst or alkaline-based solid catalyst (e.g metal oxides) tend to initiate the soap generation during the reaction when oil sources contain water and free fatty acids and deactivated the catalyst [7]. Consequently, dewatering of oil sources is crucial and required to ensure the efficiency of transesterification process [25]. Moreover, chemical method has high energy